INVESTIGATION OF PHASE AND EMULSION BEHAVIOR, SURFACTANT RETENTION, AND CONDENSATE RECOVERY FOR CONDENSATE/WATER/ETHANOL MIXTURES

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DISCLAIMER

Investigation of Phase and Emulsion Behavior, Surfactant Retention, and Condensate Recovery for Condensate/Water/Ethanol Mixtures

ABSTRACT

This semi-annual technical progress report describes work performed at Morehouse College under DOE Grant No. DE-FG26-02NT15447 during the period October 01, 2002 to April 01, 2003 which covers the first six months of the project. Presently work is in progress to characterize phase and emulsion behavior for condensate/water/ethanol system. Temperature and salinity scans are planned to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexist for this system. Test matrix to perform salinity and temperature scans has been established. Supply requests to obtain hydrocarbons, surfactant, etc., were processed and supplies obtained. Current literature in the subject area, and modeling efforts that were established in our previous studies to predict electrical conductivities and inversion phenomena were reviewed. Based on the review a computer model to predict electrical conductivities of the ethylbenzene (that has the equivalent carbon number of the condensate) / water/ ethanol system is being developed. These activities resulted in one published conference abstract during this reporting period.

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INTRODUCTION

The Department of Energy has been sponsoring fundamental and applied research in the natural gas recovery area. Recently, NETL/Pittsburgh has been interested in research focussing on innovative methods for technologies towards improved gas and condensate recovery. If an effective method can be found, the potential for incremental recovery is great.

The major factors causing hydrocarbon losses in a reservoir during production of gas and gas condensate fields are related to pressure depletion, retrograde condensation, and water encroachment. The most widespread and simple method of producing gas and gas condensate fields is by depletion, utilizing the natural reservoir pressure only. The major disadvantage of the method is the low condensate recovery. The ultimate condensate recovery from gas condensate fields is 30 - 60 %, depending on the initial content of condensate in gas. In comparison, the final recovery of gas in dry gas fields can be up to 95 %. Despite the low recovery of condensate associated with natural depletion, this method is still widely used in the majority of gas condensate fields in the world. The reasons for this are both technological and economic. Achieving increased production in partially depleted gas and gas condensate fields is essential for many gas producing companies. Incremental production can be very profitable especially in industrially developed countries. Worldwide, the potential for production and improved recovery from gas condensate fields is considerable. In order to improve the recovery from gas condensate fields innovative methods are required.

Depletion of reservoir pressure leads to a reduction in flow capacity and normally causes retrograde condensation. Offsetting the reduced flow capacity by lowering the bottom hole flowing pressure can result in near wellbore retrograde condensation, which leads to decreased effective permeability and additional reduction of flow rates. Lower production rates leads to earlier abandonment resulting in lower ultimate recovery. Significant amounts of condensate can accumulate in the near wellbore zone due to the large pressure drop in this zone. This condensation takes place in addition to the condensation within the reservoir caused by the general pressure depletion. As a result of this condensate accumulation, liquid saturations in the near wellbore zone can considerably exceed the average value over the reservoir as a whole. This causes a large reduction in well productivity. The reduction of well productivity caused by near wellbore accumulation of retrograde condensate has been observed at many fields in the USA, Russia, and Canada. At these fields the well productivity decrease reached 50% in some productive intervals due to condensate accumulation. Further pressure reduction down to the pressure of maximum condensation results in increased volume of condensed liquid. Then the mixture enters a range of direct evaporation and will result in further decrease of pressure. Pressure depletion below the dew-point pressure causes retrograde condensation throughout the entire system that leads to greater than 50% reduction in well productivity.

Water encroachment into a gas or gas condensate reservoir has two opposite effects: 1)maintenance of reservoir pressure, and 2)trapping gas and condensate behind the water level at higher pressure than by depletion and thus reduceing the recoverable reserves. Selective water encroachment in a reservoir and breakthrough of water to production wells result in an accumulation

of water in wells and their premature shut-in at higher formation pressures. The impact of each of the above mentioned factors on production and ultimate recovery of condensate and gas varies from reservoir to reservoir, but water encroachment is observed at all gas condensate fields to a certain degree. Application of surfactant flooding technology that is used in the Enhanced Oil Recovery technology may hold great potential for the improved recovery of condensate from the water encroached gas and condensate fields. For this, a research project aimed at understanding the emulsions formed by water, condensate, and a cosurfactant such as ethanol would provide valuable information including how to reduce the interfacial tension between encroaching water and condensate, and under what conditions and how this can be used towards improved recovery. The use of ethanol as the surfactant in this project would also provide valuable information on how to remove the condensate from near the wellbore by reducing the interfacial tension between the gas and condensate and hence improve the gas flow from condensate accumulated wellbores.

Application of surfactants and hence formation of emulsions depend on the desired morphology, for example, a "condensate -in-water" or a "water-in-condensate" emulsion. Formation of the "wrong" morphology or inversion from the desired morphology to the "wrong" morphology causes the product or process to fail. Mixtures of water, condensates, amphiphiles, and salt may separate into three coexisting liquid phases within a well defined temperature interval, the mean temperature of which depends sensitively but systematically on the nature of the condensate and the amphiphile and on the salt concentration. At the mean temperature of this interval one finds--for thermodynamic reasons--a maximum of the mutual solubility between water and condensate and a minimum of the interfacial tension between the aqueous and the condensate-rich phase. Both of these properties are of considerable interest for both research and industrial application.

Many, if not most, of the two-phase emulsions that may commonly exist at various temperatures in systems of surfactant, condensate, and water form in systems that also can form [1] triconjugate condensate-rich top phase (T), water-rich bottom phase (B), and middle-phase microemulsion (M). For such systems, two-phase emulsions may form in any of the various two-phase regions [2-3] that surround a stack of tie triangles in the triangular-prismatic phase diagram. For temperatures between Tlc and Tuc--the range over which phases T, M, and B coexist--there are three two-phase regions and thus six nonmultiple, two phase emulsion morphologies [4]. For such systems the plotting of phase boundaries and of boundaries between different emulsion morphologies in accordance with the phase rule introduces a rigorous way of showing how the occurrence of each of the six two-phase morphologies depends on temperature and composition. For the limiting tie lines (i.e., the sides of the tie triangle), where the three-phase and two-phase regions meet, the six two-phase morphologies will be formed by the triconjugate phases taken pairwise: T/M, M/T; B/T, T/B; and M/B, B/M [5].

One of the most widely observed phenomena of emulsion inversion is inversion hysteresis [6]. For example, the phase volume fractions at which the inversions A/B to B/A and B/A to A/B occur are somewhat different. If the pair of phase volume fraction points at which the pair of conjugate inversions occur are measured at different temperatures, the resulting measurements form a pair of inversion hysteresis lines in phase volume fraction-temperature space. The fractional phase volume

at which inversion occurs is believed to depend on many different factors, such as the temperature, structure and concentration of the emulsifying amphiphile, salinity, and hydrocarbon composition. The factors that control dispersion morphology and inversion are now well understood [5]. Qualitatively, dispersion inversion has long seemed to be a catastrophic event. The properties of an A/B (A-in-B) dispersion are very different from the properties of a B/A (B-in-A) dispersion, and the inversion from one morphology to the other is often abrupt and irreversible. Inversion is marked by a sudden change in the physical properties (e.g., electrical conductivity) of the dispersion, indicating an abrupt change in the structure of the dispersion [5]. Smith et al. [5,7-10] demonstrated for several oil/water/surfactant systems that elementary catastrophe theory provides a unifying framework to explain these phenomena in systems of variable oil/water ratio and amphiphile concentration at constant temperature and pressure. Smith et al. [1] hypothesized that wherever a phase critical point occurs, there will be a "critical point" for dispersion inversion, also; that is, pairs of dispersion inversion hysteresis lines meet at a point, and this point coincides with the critical point for the two phases of the dispersion.

Sampath et al. [5] determined the morphologies and phase volume fractions at which inversion occurred for (macro)emulsions formed by the middle-phase microemulsion (M) and water-rich bottom phase (B) by means of electrical conductivity measurements for the chemical system C6H13(OC2H4)2OH/n-tetradecane/aqueous 10mM NaCl at temperatures from 25 EC down to 12 EC, near the lower critical end-point temperature (Tlc = 10.4 EC). The M/B and B/M morphologies and their inversion hysteresis lines were found to conform to the previously postulated dispersion morphology diagram; that is, within experimental uncertainties, the two emulsion inversion lines in phase volume-temperature space met at a "critical point"' that coincided with the lower critical end point for the phases.

The phase behavior, interfacial tension and solution physical parameters only define a single interface in the condensate recovery process, the water-condensate interface. In a condensate and water filled reservoir system, two other interfaces exist, the condensate-rock and water-rock interface. The effect of these two interfaces on the condensate recovery process are just as important, if not more important, than the water-condensate interface [11-14]. Linear and radial corefloods are used to test the effect of the two rock interfaces on the condensate recovery potential of the surfactant systems. Linear corefloods provide adsorption coefficients of chemical onto the rock surface and define fluid rheology as the ability of the solution to flow through porous media. Radial corefloods to estimate condensate recovery potential are preferable to linear corefloods for a number of reasons [11-16]. The pore volume of a radial core is greater than that of a linear core making measurement of the injected and produced fluids volumes more accurate. The flow patterns in a radial core allow expansion of the interface between the injected surfactant and the fluid in the core to occur in a similar manner as in a vertical well in the field. When fractional pore volumes of chemical are injected, chemical banks thin in a manner analogous to a vertical well in the field allowing dispersion, dilution, and other potentially deleterious effects to occur. Recently, Moeti, Sampath, Smith, and Pitts [17-19] investigated the suitability of hybrid (ionic and nonionic) surfactants for enhanced oil recovery and observed inversion hystereses but lower surfactant and hydrocarbon recovery for these surfactants.

To this end, applying our experimental and modeling capabilities in the emulsion research [5,17-19], this project seeks to characterize the phase and morphology behavior of ethylbenzene that has the equivalent carbon number of condensate condensate when mixed with water and a cosurfactant such as ethanol and develop a database for use in improved condensate recovery from water encroached wells. Detailed information on optimal salinity, temperature, emulsion morphologies including inversion hystereses, lower and upper critical points, and adsorption coefficient and recovery efficiency will be obtained for ready use in actual field operations. The information to be obtained will also be useful in evaluating the use of ethanol as the surfactant to remove the condensate from near the wellbore to improve the gas flow in condensate accumulated wellbores.

The specific objectives are:

1) Perform salinity and temperature scans scans to obtain optimal salinity and temperature at which all three phases coexist.

2) Perform emulsion morphology and coreflooding experiments for the ethylbenzene/water/ethanol system that gives the best results in objective 1.

Experiments and analyses are being carried out to meet the project objectives. Objectives 1 and phase work will be accomplished by Morehouse. Coreflooding experiments will be accomplished by Surtek, our industrial partner in this project. The successful accomplishment of the objectives will provide a detailed and unique database for use in improved condensate recovery from water encroached wells.

EXECUTIVE SUMMARY

In this semi-annual report, the work performed under DOE Grant No. DE-FG26-02NT15447 during the period October 01, 2002 to April 01, 2003 which covers the first six months of the project is described and the major accomplishments are highlighted summarizing the most important research results.

Many surfactants will simultaneously form three coexisting liquid phases when mixed with condensate and water within a well defined salinity and temperature interval. At the mean temperature of this interval one finds--for thermodynamic reasons--a maximum of the mutual solubility between water and condensate. The middle phase, which contains the greatest concentration of surfactant, is called a microemulsion. Typically the microemulsion reduces the interfacial tension between condensate and water by about three or four orders of magnitude. These ultralow tensions allow the condensate-rich (top) phase to be pushed through porous media by the aqueous (bottom) phase, and the three liquid phases flow as macroemulsions. The microemulsion phase can also form two-phase, or three-phase, macroemulsion structures or morphologies when mixed with either one, or both, of the other two phases, depending on the temperature, relative volumes of the phases, and other factors. Formation of a wrong morphology or inversion from the desired morphology to the wrong morphology is also possible. Investigation of these morphologies, when they occur, and their flow through porous media are of considerable interest for both research and industrial application.

This project seeks to characterize phase and emulsion behavior, surfactant retention, and condensate recovery for condensate/water/ethanol systems. The successful accomplishment of the objectives will provide information on the role of optimal salinity, temperature, surfactant adsorption, coreflooding, and inversion hysteresis of the conjugate emulsion phases for this chemical system. This information will be useful for incremental hydrocarbon recovery during the late period of the production of gas and gas condensate fields.

Presently work is in progress to characterize phase and emulsion behavior for condensate/water/ethanol system. Temperature and salinity scans are planned to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexist for this system. Test matrix to perform salinity and temperature scans has been established. Supply requests to obtain ethylbenzene that has the equivalent carbon number of the condensate, ethanol, etc., were processed and supplies obtained. Current literature in the subject area, and modeling efforts that were established in our previous studies to predict electrical conductivities and inversion phenomena were reviewed. Based on the review, a computer model to predict electrical conductivities for ethylbenzene/water/ethanol systems is being developed. These activities resulted in one published conference abstract during this reporting period. Following the measurements of the optimal salinity and temperature, core flooding measurements will be conducted on the optimal system by our industrial partner, Surtek, CO, to characterize surfactant retention and condensate recovery.

EXPERIMENTAL

Presently work is in progress to characterize phase and emulsion behavior for condensate/water/ethanol system. Temperature and salinity scans are planned to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexist for this system.

Test matrix to perform salinity and temperature scans has been established to identify the optimal salinity and temperature, and the temperature and salinity intervals in which all three phases coexist for this chemical system. About 10 samples of equal volume of ethylbenzene and water with initially 2% concentration of surfactant will be tested for optimal salinity by varying the salinity with NaCl from 1 to 10%, or greater. The temperature of the water bath in these experiments will be set at 20, 25, 30, and 35 EC. Following the salinity experiments, measurements will be made with zero salinity or 10 mm NaCl in water for various surfactant concentrations. The small salt concentration may be used to improve the sensitivity and accuracy of the conductivity measurements by increasing the conductivity differences between the conjugate phases of the emulsions. The resulting temperature vs. surfactant concentration plot will yield a typical alpha shape curve that will demonstrate the existence of 1, 2, or 3 phases in the system. The best ethylbenzene/water/ethanol system defined by the above phase work will then be studied for core flooding, and emulsion morphologies. Core flooding measurements will be conducted by our industrial partner, Surtek, CO, to characterize surfactant retention and oil recovery. Measurements for emulsion morphologies will be performed by Morehouse. Briefly, electrical conductivities will be measured for top/bottom, top/middle, and middle/bottom phases that form the sides of the tie triangle diagram by mixing measured volumes of the pre-equilibrated phases. The activities performed resulted in one published conference abstract during this reporting period.

RESULTS AND DISCUSSION

During this reporting period, supply requests to obtain hydrocarbons such as ethylbenzene, and surfactants such as ethanol, etc., were processed and supplies obtained. Our Industrial partner Surtek was contacted to obtain condensate. Surtek tried with its business clients. One such client company in Texas was willing to provide Morehouse with some condensate, however, it was not possible for them to ship the condensate from Texas to Atlanta because no mail services like UPS accept the shipment for delivery due to the flamable nature of the product. Current literature in the subject area [1-23], and modeling efforts that were established in our previous studies [5,7,9-10,17-23] to predict electrical conductivities and inversion phenomena were reviewed. Based on the review a computer model to predict electrical conductivities of the ethylbenzene (that has the equivalent carbon number of the condensate) / water/ ethanol system is being developed.

Outcome of this Period

1. Sampath, R., Moeti, L., and Dixon, R., Investigation of Phase and Emulsion Behavior, Surfactant Retention, and Condensate Recovery for Condensate/Water/Ethanol Mixtures,

Historically Black Colleges and Universities and Other Minority Institutions Contractors Review Meeting, June 3-4, 2003, Pittsburgh, PA.

Plans for the next Reporting Period

Salinity and temperature scans are scheduled to be completed within the next reporting period.

CONCLUSION

The project is progressing well. Chemical supplies were obtained. Literature related to the conductivity modeling efforts of the emulsion system were reviewed. Test matrix for salinity and temperature scans were established. These activities resulted in one conference abstract during this period. Experimental set up for salinity and temperature scans is in progress.

ACKNOWLEDGMENTS

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